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(71) Applicant: **KANEGAFUCHI KAGAKU KOGYO KABUSHIKI KAISHA**, 2-4 Nakanoshima 3-chome, Kita-ku Osaka-shi Osaka-fu (JP)

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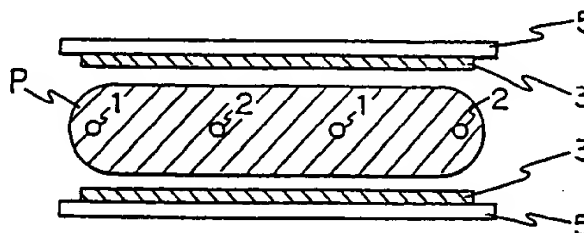
(72) Inventor: **TAWADA, Yoshihisa**, 14-39, Oikemiyamadae Kita-ku, Kobe-shi, Hyogo 651-11 (JP)  
Inventor: **TSUGE, Kazunori**, 9-30-1220, Maikodai 2-chome, Tarumi-ku, Kobe-shi Hyogo 655 (JP)

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(74) Representative: **Gille, Christian**, Dipl.-Ing. et al, Türk & Gille Bruckner Strasse 20, D-4000 Düsseldorf 13 (DE)

### (54) FILM FORMING METHOD AND APPARATUS.

(57) A method of forming films by glow discharge decomposition, characterized in that one or a plurality of rows of electrode pairs, each of which rows consists of a plurality of linearly-arranged high-frequency electrode pairs, are placed in order, substrates being arranged on both sides of the electrode pair arrays so that the former are substantially parallel to the latter. According to this method, the possibility of a film being damaged by plasma can be minimized, and the shield on the rear sides of RF electrodes can be omitted. Moreover, this method enables the formation of a film of a large area.



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**TITLE MODIFIED**

**DESCRIPTION**

see front page

**TITLE MODIFIED**

FILM FORMING PROCESS AND  
APPARATUS USED THEREFOR

see front page

5

**TECHNICAL FIELD**

The present invention relates to a process for forming semiconductor film and an apparatus used therefor.

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**BACKGROUND ART**

Heretofore, glow discharge decomposers used for the production of solar cells and the like have been mostly employed in the form of an apparatus based on a parallel-plate method shown in Fig. 4. The parallel-plate method is suitable for the formation of films of large area but has a disadvantage that an electric discharge taking place between an RF electrode 6 and an opposed electrode 7 results in the plasma damaging of a thin film formed on a substrate 3 placed on the RF electrode or the opposed electrode (ground electrode). Moreover, since an electric discharge also takes place on the back of the RF electrode 6 forming the RF electrode pair, it is necessary to provide a shield for suppressing this discharge. However, the provision of such a shield has the disadvantage of making the discharge unstable.

Hamakawa et al. proposed a transverse plasma method (Japanese Examined Patent Publication (Tokkyo Kokoku) No. 42126/1983), as shown in Fig. 5, to minimize damage caused by plasma to thin films formed. However, there is naturally a limit to the distance between the RF electrode 6 and the ground electrode 7, and hence to the size of the substrate 3 to be used, which results in a disadvantage that it is impossible to obtain a thin film of large area. Moreover, in order to avoid deposition of a thin film on the electrode pair, a container such as one designated by the numeral 4 is required.

In view of the actual circumstances described

above, the present inventors have conducted intensive research to minimize damage caused by plasma to a thin film formed on the substrate in the parallel-plate method and to dispense with the shield required on the back of the RF electrode and the container used in the transverse plasma method while forming a thin film of large area, and have found out that the object can be attained by the present invention, and then have completed the present invention.

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## DISCLOSURE OF THE INVENTION

Namely, the present invention relates to a process for forming a film, characterized in that, in forming a thin film of amorphous semiconductor or the like by the glow discharge decomposition, one or more electrode pair rows each consisting of a plurality of high frequency electrode pairs arranged in a line are arranged in parallel and substrates are arranged on both sides of the electrode pair row approximately in parallel to the electrode pair row, and relates to a glow discharge decomposition film forming apparatus, characterized by comprising one row or more parallel rows each consisting of a plurality of high frequency electrode pairs arranged in a line, substrate moving devices disposed on both sides of the electrode pair row to arrange substrates approximately in parallel to the electrode pair row, and, if necessary, a heater positioned to heat the substrate.

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## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an explanatory view showing an embodiment of the apparatus of the present invention; Fig. 2 is an explanatory view showing an embodiment of the high frequency electrode pair row used in the apparatus of the present invention; Fig. 3 is an explanatory view showing another embodiment of the apparatus of the present invention; and Figs. 4 and 5 are explanatory views of film forming apparatuses conventionally used.

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## BEST MODE OF THE INVENTION

The process of the present invention is described with reference to Fig. 1 showing an embodiment of the apparatus of the invention in the following.

5           As shown in Fig. 1, high frequency electrodes 1 and 2 are linearly and alternately arranged in a plurality of pairs, so that electric discharge takes place between the electrodes 1 and 2. The electrodes may be planar, but in order to prevent abnormal  
10 discharge and to produce uniform plasma P, it is preferable that the electrodes have round cross-section, e.g., circular or oval. Such a construction makes unnecessary the shield on the back which is required in the case of planar electrodes. The distance between the  
15 electrodes is preferably about 5 to 50 cm from the standpoint of stability and uniformity of discharge, more preferably about 10 to 40 cm. Only a pair of electrodes 1 and 2 may be provided or, as shown in Fig. 1, a number of pairs may be arranged in a line. If a number of  
20 electrode pairs are arranged in a line, the area of the film to be formed can be increased, theoretically to infinitude. On the other hand, with the parallel-plate method, the maximum area of electrode is limited to about 1 m<sup>2</sup>. As shown in Fig. 3, if a plurality of rows each  
25 consisting of a number of the electrode pairs arranged in a line are arranged in parallel, the film forming rate can be increased. In addition, a concrete example in which the high frequency electrode pairs are arranged is shown in Fig. 2.

30           On both sides of the electrode pair row are substrate moving devices (not shown) for moving the substrates 3 in parallel to the electrode pair row. The substrate moving device may have a function so as to carry the substrate 3 to the electrode pair section, and  
35 then to move them after the film formation. However, it is preferable that while maintaining the distance between the substrate and the electrode pair row approximately constant during film formation, the substrate is

subjected to movement in one direction or to repetitive amplitude-movement (preferable amplitude being at least 1/4 of the distance between the electrode pairs). If the substrate is moved during film formation in this manner, the distribution of the thickness of the film formed can be minimized. For continuous formation of films by using a long continuous substrate, the method of moving the substrate in one direction is suitable, while for batch-wise film formation by using a short substrate, the method of repetitively amplitude-moving the substrate is suitable. A short substrate may, of course, be continuously moved. In the conventional manner, if the substrate deviates from the discharge section, matching would be out of order, which requires a special provision.

According to the process of the present invention, electric discharge is stabilized even if the substrate is deviated from the discharge section, because no discharge takes place through the substrate.

A heater 5 which is provided according to the requirement to heat the substrate 3 may be used to heat the substrate 3. A temperature of the substrate varies depending on the type of films to be formed and the purpose of use, and usually preferably about 50° to 400°C.

The above-mentioned apparatus of the present invention and shown in Fig. 1 is installed in a glow discharge decomposition film forming apparatus for preparing an amorphous semiconductor film or the like. When forming a film of about 0.01 to 100  $\mu\text{m}$  in thickness, there are employed a frequency of about 1 KHz to 100 MHz, and an RF power per unit area of film of 0.01 to 10  $\text{W}/\text{cm}^2$ , when microcrystallizing, about 1 to 100  $\text{W}/\text{cm}^2$ , in the presence of about 0.01 to 5 Torr of raw material gas comprising a reactive gas such as a silicon compound, a carbon compound, a nitrogen compound, a doping gas or an inert gas.

One of the high frequency electrodes 1 and 2 may be grounded, but none of them may be grounded so that

they are not distinguished from each other as to which is plus or minus (floated). In the case where the high frequency electrodes 1 and 2 are floated, there is advantages that plasma is uniform and that less discharge  
5 takes place between the substrate and an inner wall of the apparatus.

The row of high frequency electrodes 1 and 2 and the substrates 3 transferred on both sides thereof may, if approximately parallel, be horizontal, vertical  
10 or inclined at any angle. In case of substantially vertical arrangement, a good film is formed since there is no possibility of dust falling onto the film formed.

There are no particular limitation with respect to the apparatus for forming an amorphous semiconductor  
15 film or the like having the apparatus of the present invention installed therein. Thus, any type of film forming apparatus which is usually used may be employed. For example, the apparatus may be of multi-chamber construction. In such a case the apparatus of the  
20 present invention may be installed in at least one of the chambers constructing the multi-chamber construction (for instance, one of the chambers forming a p-layer, an i-layer or an n-layer). In the case where the apparatus of the multi-chamber construction is used, each partition  
25 wall is provided with a slit and a gate valve to allow the substrate to pass through the individual chambers. However, it is preferable from the standpoint of increased productivity that the slit and a differential exhaust chamber instead of the gate valve are provided to  
30 allow continuous movement.

The production of a film according to the process of the present invention by using the apparatus device of the invention has characteristics such that less damage is caused by plasma, a film of high quality  
35 is formed at a high rate, less powder is formed, and a film having fewer pinholes can be formed since parasitic discharge is less generated, a film of large area can be easily formed, and a decomposition product is effectively

deposited on the substrate. Furthermore, in the case of such elements and devices as solar cells of silicon-containing pin, pn, hetero- or homo-type, sensors, IFT (thin film transistor), and CCD (charge coupled device).  
5 Particularly in the case of amorphous silicon-containing solar cells, a film of large area having a conversion efficiency of not less than 10 % is obtained according to the present because an efficiency of such devices is greatly influenced by plasma damage. Further, the film  
10 prepared according to the present invention can also be satisfactorily applicable to electronic photographic light-sensitive materials, LSI passivation films and printed circuit board insulation films.

The present invention is explained by means of  
15 Examples.

#### Example 1

In the arrangement of Fig. 1, electrodes (10 mm in diameter and 500 mm in length) were arranged at  
20 intervals of 150 mm, and RF was introduced into the electrodes through a 13.56 MHz RF oscillator and the matching circuit shown in Fig. 2. By using ITO/SnO<sub>2</sub> glass substrates of 40 cm square having a temperature of 200°C, there were formed an 100 Å thick p-layer from  
25 SiH<sub>4</sub>/CH<sub>4</sub> = 50/50 and B<sub>2</sub>H<sub>6</sub>/(SiH<sub>4</sub> + CH<sub>4</sub>) = 0.05 % (% by mole, hereinafter the same), a 6000 Å thick i-layer from SiH<sub>4</sub> and a 500 Å thick n-layer from PH<sub>3</sub>/SiH<sub>4</sub> = 0.2 %. Subsequently, an Al layer of about 1000 Å in thickness was formed by vapor deposition. As a result of testing  
30 the distribution of conversion efficiency of the solar cell by using an AM-1 100 mW/cm<sup>2</sup> solar simulator, the minimum conversion efficiency was 10.4 %, the maximum was 11.7 % and the average was 11 %, which proved that the solar cell was very uniform and had a high efficiency.  
35 Further, even if films were formed at a growth rate of 20 Å/sec, the efficiency of the cell obtained was not almost changed.



## Example 2

In the arrangement of Fig. 3, electrodes (10 mm in diameter and 500 mm in length) were arranged at intervals of 150 mm, and RF was introduced into the electrodes through a 13.56 MHz RF oscillator and three matching circuits shown in Fig. 2. The RF power was 120 W. By using ITO/SnO<sub>2</sub> glass substrates of 40 cm square having a temperature of 200°C, there were formed an 100 Å thick p-layer under the conditions of 150 sccm of SiH<sub>4</sub>, 150 sccm of CH<sub>4</sub>, and 150 sccm of B<sub>2</sub>H<sub>6</sub> diluted with H<sub>2</sub> to 1000 ppm, a 6000 Å thick i-layer under the conditions of 240 sccm of SiH<sub>4</sub>, and a 500 Å thick n-layer under the conditions of 150 sccm of SiH<sub>4</sub> and 300 sccm of PH<sub>3</sub> diluted with H<sub>2</sub> to 1000 ppm. Subsequently, an Al layer of about 1000 Å was formed by vapor deposition. As a result of testing the distribution of conversion efficiency of the solar cell by using an AM-1 100 mW/cm<sup>2</sup> solar simulator, the minimum conductive efficiency was 10.1 %, the maximum was 11.9 % and the average was 10.8 %, which proved that the solar cell was very uniform and had a high efficiency.

## CLAIM

1. A process for forming a film, characterized in that, in forming a film by glow discharge decomposition, one or more electrode pair rows each consisting of a plurality of high frequency electrode pairs are arranged in a line and in parallel and substrates are arranged on both sides of said electrode pair row approximately in parallel to the electrode pair row.

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2. The process of Claim 1, wherein said substrate is moved while the distance between the substrate and the electrode pair row is maintained.

15

3. The process of Claim 2, wherein the movement is a repetitive amplitude movement.

4. The process of Claim 2, wherein the movement is a movement in one direction.

20

5. The process of Claim 1, wherein the high frequency electrodes are electrodes which are not distinguishable from each other as to which is plus or minus (being floated).

25

6. The process of Claim 5, wherein the high frequency electrodes are circular or oval in cross section.

30

7. The process of Claim 1, 2, 3, 4, 5 or 6, wherein a frequency of a high frequency wave is 1 KHz to 100 MHz.

8. A glow discharge decomposition film forming apparatus, characterized by comprising one row or a plurality of parallel rows each consisting of a plurality of high frequency electrode pairs arranged in a line, and substrate moving devices disposed on both sides of the

35

electrode pair row approximately in parallel to the  
electrode pair row.

5 The apparatus of Claim 8, wherein said  
substrate moving device is adapted to move the substrate  
while the distance between the substrate and the  
electrode pair row is maintained.

10 The apparatus of Claim 8, wherein the  
movement is a repetitive amplitude movement.

11. The apparatus of Claim 10, wherein the  
amplitude of said amplitude movement is at least 1/4 of  
the distance between electrode pairs.

15 12. The apparatus of Claim 8, wherein the  
movement is a movement in one direction.

20 13. The apparatus of Claim 8, 9, 10, 11 or 12,  
wherein the high frequency electrodes are electrodes  
which are not substantially from said substrate to which  
is plus to minus (being treated).

25 14. The apparatus of Claim 13, wherein the high  
frequency electrodes are circular or oval in cross  
section.

30 15. The apparatus of Claim 8, 9, 10, 11, 12, 13  
or 14, wherein a frequency of a high frequency wave is 1  
KHz to 100 MHz.

16. The apparatus of Claim 8, which comprises a  
heater for heating the substrate.

35 17. The apparatus of Claim 8, wherein the film  
forming apparatus has a main-chamber and a side film.

18. The apparatus of Claim 17, wherein the

multi-chamber construction is a construction in which the chambers are partitioned by partition walls each having a slit and the partitioned chambers are differentially exhausted.

FIG. 1

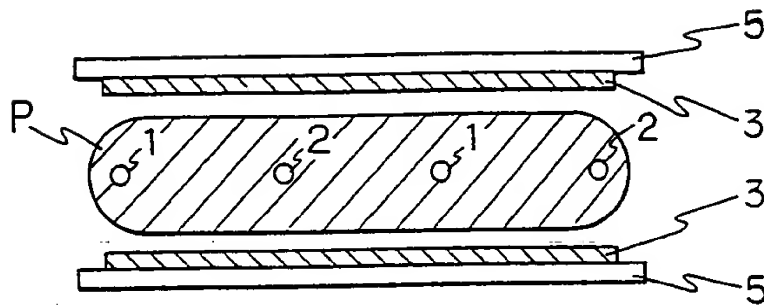


FIG. 2

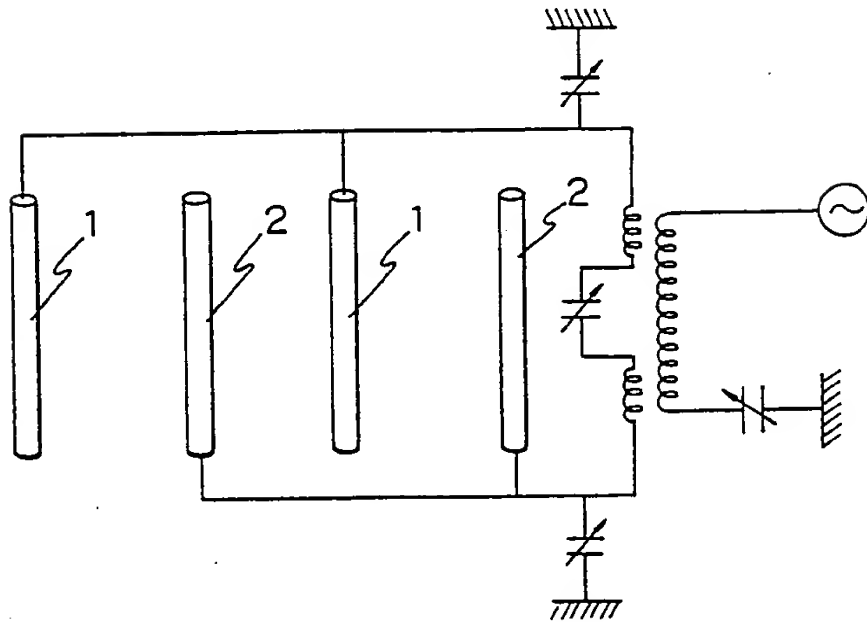


FIG. 3

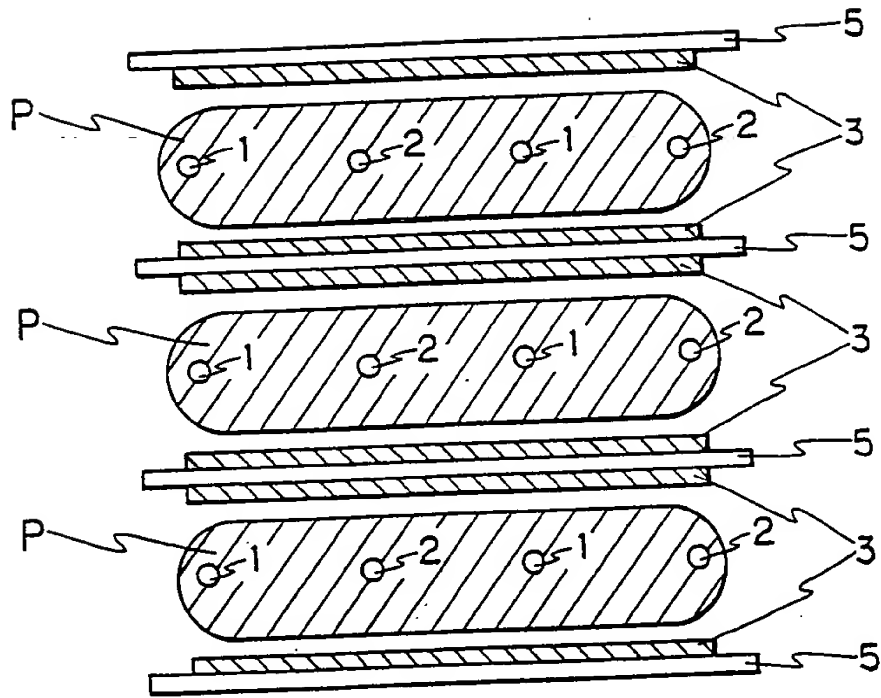


FIG. 4

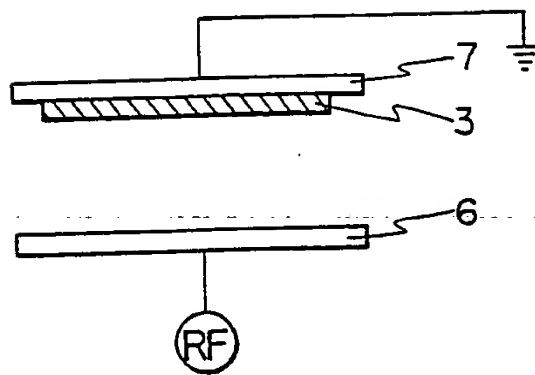
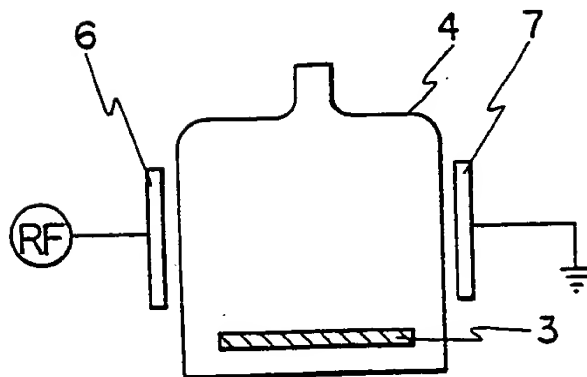


FIG. 5



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP85/00066

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<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. <sup>4</sup> H01L 21/205, H01L 31/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>5</sup>		
Classification System	Classification Symbols	
IPC	H01L 21/205, H01L 31/04	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>6</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>7</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>16</sup>
Y	JP, A, 58-116727 (Suwa Seikosha Kabushiki Kaisha) 12 July 1983 (12. 07. 83) (Family nashi)	1 - 18
Y	JP, A, 52-122478 (Toshiba Corp.) 14 October 1977 (14. 10. 77) (Family nashi)	1 - 18
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<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>19</sup>		Date of Mailing of this International Search Report <sup>1</sup>
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